



(12)

**EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 158(3) EPC

(21) Application number: 87907676.8

(51) Int.Cl.: C 08 F 10/00  
C 08 F 4/64

(22) Date of filing: 19.11.87

Data of the International application taken as a basis:

(86) International application number:  
PCT/JP87/00898

(87) International publication number:  
WO88/03532 (02.06.88 88/12)

(30) Priority: 20.11.86 JP 275191/86

(40) Date of publication of application:  
26.07.89 Bulletin 89/30

(64) Designated Contracting States:  
AT DE FR GB IT NL

(71) Applicant: MITSUI PETROCHEMICAL INDUSTRIES, LTD.  
2-5, Kasumigaseki 3-chome Chiyoda-ku  
Tokyo 100(JP)

(72) Inventor: TSUTSUI, Toshiyuki  
3-6, Misono 1-chome Otake-shi  
Hiroshima 739-06(JP)

(72) Inventor: TOYOTA, Akinori  
103-21, Minamiwakuni-cho 2-chome Iwakuni-shi  
Yamaguchi 740(JP)

(72) Inventor: KASHIWA, Norio  
2-9, Muronoko-cho 1-chome Iwakuni-shi  
Yamaguchi 740(JP)

(74) Representative: Myerscough, Philip Boyd et al.  
J.A.Kemp & Co. 14, South Square Gray's Inn  
London, WC1R 5EU(GB)

(52) **PROCESS FOR POLYMERIZING OLEFIN.**

(57) A process for polymerizing olefin, which comprises using a catalyst composed of a compound of transition metal of the group IVB of the periodic table, such as zirconium, aluminoxane formed from trimethylaluminum, and aluminoxane wherein at least one hydrocarbyl group other than n-alkyl group is bound to the aluminum atom. This process enables polymerization of olefin with excellent polymerization activity even when the amount of aluminoxane prepared from expensive trimethylaluminum is reduced. The produced polymer has a comparatively large molecular weight.

- 1 -

## SPECIFICATION

## PROCESS FOR POLYMERIZING OLEFINS

## TECHNOLOGICAL FIELD

The present invention relates to a process for polymerizing olefins. Specifically, the present invention relates to a process for polymerizing olefins with excellent polymerization activity to produce an olefin polymer having a large molecular weight. More specifically, the present invention relates to a process for producing an olefin polymer having a narrow molecular weight distribution and, when applied to the copolymerization of at least two olefins, an olefin copolymer having a narrow molecular weight distribution and a narrow composition distribution, with excellent polymerization activity.

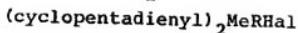
## BACKGROUND TECHNOLOGY

For the production of an alpha-olefin polymer, particularly an ethylene polymer or an ethylene/alpha-olefin copolymer, methods have previously been known in which ethylene is polymerized, or ethylene and an alpha-olefin are copolymerized, in the presence of a titanium-based catalyst comprising a titanium compound and an organoaluminum compound or a vanadium-based catalyst comprising a vanadium compound and an organoaluminum compound.

On the other hand, catalysts comprising a zirconium compound and an aluminoxane have been proposed recently as a new type of Ziegler catalyst for olefin polymerization.

Japanese Laid-Open Patent Publication No. 19309/1983 describes a process which comprises polymerizing ethylene and at least one alpha-olefin having 3 to 12 carbon atoms at a temperature of -50° to 200°C in the presence of a catalyst composed of a transition metal-containing catalyst represented by the following formula

- 2 -



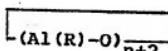
wherein R represents cyclopentadienyl, C<sub>1</sub>-C<sub>6</sub> alkyl or halogen, Me represents a transition metal, and Hal represents halogen,

- 5 and a linear aluminoxane represented by the following formula



wherein R represents methyl or ethyl, and n is the number of 4 to 20,

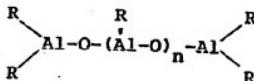
- 10 or a cyclic aluminoxane represented by the following formula



wherein R and n have the same definitions as given above.

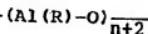
- 15 This patent document states that in order to adjust the density of the resulting polyethylene, ethylene should be polymerized in the presence of a small amount (up to 10% by weight) of a slightly long-chain alpha-olefin or a mixture thereof.

- 20 Japanese Laid-Open Patent Publication No. 95292/1984 describes an invention relating to a process for producing a linear aluminoxane represented by the following formula



- 25 wherein n is 2 to 40 and R is C<sub>1</sub>-C<sub>6</sub> alkyl, and a cyclic aluminoxane represented by the following formula

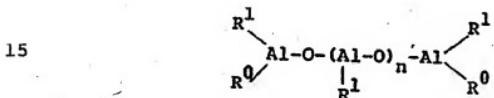
- 3 -



wherein R and n have the same definitions as given above.

This publication states that when an olefin is polymerized using a mixture of, for example, methylaluminoxane produced by the above process with a bis(cyclopentadienyl) compound of titanium or zirconium, a polyethylene is obtained in an amount of at least 25 million grams per gram of the transition metal per hour.

10 Japanese Laid-Open Patent Publication No. 35005/1985 discloses a process for producing a catalyst for polymerization of olefins, which comprises reacting an aluminoxane compound represented by the following formula



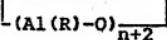
wherein  $R^1$  represents  $C_1-C_{10}$  alkyl, and  $R^0$  is  $R^1$  or is bonded to represent  $-O-$ , with a magnesium compound, then chlorinating the reaction product, and treating the chlorinated product with a 20 compound of Ti, V, Zr or Cr. The above publication describes that the above catalyst is especially suitable for the copolymerization of ethylene with a  $C_3-C_{12}$  alpha-olefin mixture.

Japanese Laid-Open Patent Publication No. 25 35006/1985 discloses a combination of (a) at least two different compounds selected from a mono-, di- or tri-cyclopentadienyl compound of transition metals or its derivative with (b) an alumoxane (an aluminoxane) as a catalyst system for blending polymers in a reactor. 30 Example 1 of this publication discloses that a polyethylene having a number average molecular weight of

- 4 -

- 15,300 and a weight average molecular weight of 36,400 and containing 3.4 mole % of a propylene component was obtained by polymerizing ethylene and propylene using bis(pentamethylcyclopentadienyl)dimethylzirconium and an alumoxane as a catalyst. In Example 2 of this publication, a blend of a polyethylene and an ethylene/propylene copolymer having a number average molecular weight of 2,000, a weight average molecular weight of 8,300 and a propylene component content of 7.1 mole % and consisting of a toluene-soluble portion having a number average molecular weight of 2,200, a weight average molecular weight of 11,900 and a propylene component content of 30 mole % and a toluene-insoluble portion having a number average molecular weight of 3,000, a weight average molecular weight of 7,400 and a propylene component content of 4.8 mole % was obtained by polymerizing ethylene and propylene using bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(methylcyclopentadienyl)-zirconium dichloride and an alumoxane as a catalyst.
- Likewise, Example 3 of this publication describes a blend of a LLDPE and an ethylene/propylene copolymer composed of a soluble portion having a molecular weight distribution ( $M_w/M_n$ ) of 4.57 and a propylene component content of 20.6 mole % and an insoluble portion having a molecular weight distribution of 3.04 and a propylene component content of 2.9 mole %.

Japanese Laid-Open Patent Publication No. 35007/1985 describes a process which comprises polymerizing ethylene alone or with an alpha-olefin having at least 3 carbon atoms in the presence of a catalyst system comprising a metallocene and a linear alumoxane represented by the following formula



- 5 -

wherein R represents an alkyl group having 1 to 5 carbon atoms and n has the same definition as given above.

The publication describes that the polymer obtained by 5 the above process has a weight average molecular weight of about 500 to about 1,400,000 and a molecular weight distribution of 1.5 to 4.0.

Japanese Laid-Open Patent Publication No. 35008/1985 describes that a polyethylene or a copolymer 10 of ethylene and a C<sub>3</sub>-C<sub>10</sub> alpha-olefin having a wide molecular weight distribution is produced by using a catalyst system comprising at least two types of metalloccenes and an alumoxane. The publication states that the above copolymer has a molecular weight distribution 15 (Mw/Mn) of 2 to 50.

Furthermore, Japanese Laid-Open Patent Publications Nos. 260602/1985 and 130604/1985 propose a process for polymerizing olefins using catalysts formed from a transition metal compound and a mixed organo- 20 aluminum compound composed of an aluminoxane and an organoaluminum compound. The publications state that the addition of the organoaluminum compound gives increased polymerization activity.

#### DISCLOSURE OF THE INVENTION

25 An object of the present invention is to provide an industrially advantageous process for olefin polymerization which can polymerize olefins using a relatively small amount of an expensive aluminoxane but with excellent polymerization activity.

30 A further object of the present invention is to provide a process for producing an olefin homopolymer having a narrow molecular weight distribution or an olefin copolymer having a narrow molecular weight distribution and a narrow composition distribution, particularly an ethylene-alpha-olefin copolymer having a narrow molecular weight distribution and a narrow

- 6 -

composition distribution, with excellent polymerization activity.

A still further object of the present invention is to provide a process for olefin polymerization which 5 can provide an olefin homopolymer or copolymer as mentioned above, having a relatively large molecular weight.

Other objects and advantages of the present invention will become apparent from the following explanation. 10

These objects and advantages of the present invention can be achieved by a process for polymerizing olefins, characterized by polymerizing or copolymerizing olefins in the presence of a catalyst composed of

- 15 (A) a compound of a transition metal of Group IVB of the periodic table,  
(B) an aluminoxane produced from trimethyl-aluminum, and  
(C) an aluminoxane wherein at least one hydrocarbon group other than n-alkyl groups is bonded to an aluminum atom.
- 20

The present invention is explained in detail below.

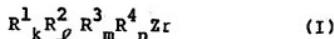
In the present invention, the term "polymerization" means in some cases not only homopolymerization 25 but also copolymerization, and the term "polymer" means in some cases not only a homopolymer but also a copolymer.

The catalyst component (A) used in the process 30 of the present invention is a compound of a transition metal of Group IVB of the periodic table. Specifically, it is a compound of a transition metal selected from the group consisting of titanium, zirconium and hafnium. The transition metal in the catalyst component (A) is preferably titanium or zirconium, especially preferably zirconium.

- 7 -

As the compound of the transition metal of Group IVB of the periodic table in the catalyst component (A), there can be mentioned a zirconium compound having a group with a conjugated  $\pi$ -electron as a ligand.

- 5 Examples of the zirconium compound having a group with a conjugated  $\pi$ -electron as a ligand are compounds represented by the following formula (I)



wherein  $R^1$  represents a cycloalkadienyl group,  $R^2$ ,  $R^3$  and 10  $R^4$  are identical or different and each represents a cycloalkadienyl group, an aryl group, an alkyl group, an aralkyl group, a halogen atom or a hydrogen atom,  $k > l$ , and  $k+l+m+n = 4$ .

15 Examples of the cycloalkadienyl group are a cyclopentadienyl group, a methylcyclopentadienyl group, an ethylcyclopentadienyl group, a dimethylcyclopentadienyl group, an indenyl group and a tetrahydroindenyl group. Examples of the alkyl group represented by  $R^2$ ,  $R^3$  and  $R^4$  are a methyl group, an ethyl group, a propyl 20 group, an isopropyl group and a butyl group. Examples of the aryl group are a phenyl group and a tolyl group. Examples of the aralkyl group are a benzyl group and a neophil group. Examples of the halogen atom are fluorine, chlorine and bromine. Examples of the 25 zirconium compound are as follows.

bis(Cyclopentadienyl)zirconium monochloride monohydride,

bis(cyclopentadienyl)zirconium monobromide monohydride,

30 bis(cyclopentadienyl)methylzirconium hydride, bis(cyclopentadienyl)ethylzirconium hydride, bis(cyclopentadienyl)phenylzirconium hydride, bis(cyclopentadienyl)benzylzirconium hydride, bis(cyclopentadienyl)neopentylzirconium

35 hydride,

- 8 -

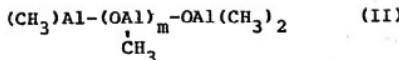
- bis(methylcyclopentadienyl)zirconium mono-  
chloride monohydrate,  
bis(indenyl)zirconium monochloride monohydrate,  
bis(cyclopentadienyl)zirconium dichloride,  
5       bis(cyclopentadienyl)zirconium dibromide,  
bis(cyclopentadienyl)methylzirconium mono-  
chloride,  
bis(cyclopentadienyl)ethylzirconium mono-  
chloride,  
10      bis(cyclopentadienyl)cyclohexylzirconium  
monochloride,  
bis(cyclopentadienyl)phenylzirconium mono-  
chloride,  
bis(cyclopentadienyl)benzylzirconium mono-  
15      chloride,  
bis(methylcyclopentadienyl)zirconium di-  
chloride,  
bis(indenyl)zirconium dichloride,  
bis(indenyl)zirconium dibromide,  
20      bis(cyclopentadienyl)diphenylzirconium,  
bis(cyclopentadienyl)dibenzylzirconium, and  
bis(cyclopentadienyl)dimethylzirconium.  
There can also be mentioned a zirconium com-  
pound having a multidentate ligand in which at least two  
25      groups selected from the group consisting of an indenyl  
group, a substituted indenyl group and its partial  
hydrogenation product are bonded to each other via a  
lower alkylene group. Examples of such a zirconium  
compound are as follows.  
30      Ethylenebis(indenyl)dimethylzirconium,  
ethylenebis(indenyl)diethylzirconium,  
ethylenebis(indenyl)diphenylzirconium,  
ethylenebis(indenyl)methylzirconium mono-  
chloride,  
35      ethylenebis(indenyl)ethylzirconium mono-  
chloride,

- 9 -

- ethylenebis(indenyl)methylzirconium mono-  
bromide,  
ethylenebis(indenyl)zirconium dichloride,  
ethylenebis(indenyl)zirconium dibromide,  
5 ethylenebis(4,5,6,7-tetrahydro-1-indenyl)di-  
methylzirconium,  
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-  
methylzirconium monochloride,  
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-  
10 zirconium dichloride,  
ethylenebis(4,5,6,7-tetrahydro-1-indenyl)-  
zirconium dibromide,  
ethylenebis(4-methyl-1-indenyl)zirconium di-  
chloride,  
15 ethylenebis(5-methyl-1-indenyl)zirconium di-  
chloride,  
ethylenebis(6-methyl-1-indenyl)zirconium di-  
chloride,  
ethylenebis(7-methyl-1-indenyl)zirconium di-  
chloride,  
20 ethylenebis(5-methoxy-1-indenyl)zirconium  
dichloride,  
ethylenebis(2,3-dimethyl-1-indenyl)zirconium  
dichloride,  
25 ethylenebis(4,7-dimethyl-1-indenyl)zirconium  
dichloride, and  
ethylenebis(4,7-dimethoxy-1-indenyl)zirconium  
dichloride.

The catalyst component (B) used in the process  
30 of the present invention is an aluminoxane produced from  
trimethylaluminum. It is specifically an aluminoxane  
produced from the reaction of trimethylaluminum with  
water. Examples of the aluminoxane used as the catalyst  
component (B) are organoaluminum compounds represented by  
35 the following general formula (III)

- 10 -



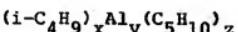
wherein  $m$  is the number of 2 or larger, preferably 5 or larger, especially preferably 6 to 40.

The catalyst component (C) used in the process of the present invention is an aluminoxane wherein at least one hydrocarbon group other than n-alkyl groups are bonded to an aluminum atom.

The aluminoxane is specifically an aluminoxane produced from the reaction of an aluminum compound having at least one hydrocarbon group other than n-alkyl groups with water. Examples of the hydrocarbon groups other than n-alkyl groups are branched alkyl groups (e.g. iso-alkyl), cycloalkyl groups and aryl groups. Specific examples of the aluminum compound are trialkylaluminums such as triisopropylaluminum, triisobutylaluminum, tri-2-methylbutylaluminum, tri-3-methylbutylaluminum, tri-2-methylpentylaluminum, tri-3-methylpentylaluminum, tri-4-methylpentylaluminum, tri-2-methylhexylaluminum, tri-3-methylhexylaluminum and tri-2-ethylhexylaluminum; tricycloalkylaluminums such as tricyclohexylaluminum; triarylaluminums such as triphenylaluminum and tri-tolylaluminum; dialkylaluminum hydrides such as diisobutylaluminum hydride; and alkyl aluminum alkoxides such as isobutylaluminum methoxide, isobutylaluminum ethoxide and isobutylaluminum isopropoxide. Of these organo-aluminum compounds, there are preferred aluminum compounds having at least one branched alkyl group, particularly trialkylaluminum compounds. There are also

- 11 -

preferred isoprenylaluminums represented by the general formula



wherein X, y and z are each a positive integer  
5 of  $z \geq 2x$ .

The catalyst components (B) and (C) can be produced by, for example, the following methods.

(1) A method which comprises suspending a compound containing water of adsorption or a salt containing water of crystallization, such as magnesium chloride hydrate, copper sulfate hydrate, aluminum sulfate hydrate, nickel sulfate hydrate or cerous chloride hydrate in a hydrocarbon, and reacting it with a trialkylaluminum.

15 (2) A method which comprises reacting a trialkylaluminum directly with water in a medium such as benzene, toluene, ethyl ether or tetrahydrofuran.

It is preferred to adopt the method (1). Incidentally, the catalyst components (B) and (C) may 20 contain a small amount of an organometallic component.

In the process of the present invention, the catalyst components (A), (B) and (C) may be separately fed into the reaction system. Or, it is possible to add a premixture of any two of the above components and the 25 remaining one catalyst component separately into the reaction system. Alternatively, all of the catalyst components (A), (B) and (C) may be premixed and then fed into the reaction system. When two catalyst components are to be mixed in advance, the catalyst components to be 30 mixed are preferably the catalyst components (A) and (B).

In the premixing of the catalyst components (A) and (B), the concentration of the transition metal atom is usually  $2.5 \times 10^{-4}$  to  $1.5 \times 10^{-1}$  milligram-atom/liter, preferably  $5.0 \times 10^{-4}$  to  $1.0 \times 10^{-1}$  milligram-atom/liter.

- 12 -

The concentration of the aluminoxane is usually 0.05 to 5 gram-atoms/liter, preferably 0.1 to 3 gram-atoms/liter, as Al atom. The temperature in the premixing is usually -50° to 100°C, and the mixing time is usually 0.1 minute 5 to 50 hours.

The amount of the transition metal compound (A) at the time of preforming the process of the present invention is, in terms of the concentration of the transition metal atom in the polymerization reaction system, 10  $10^{-8}$  to  $10^{-2}$  gram-atom/liter, preferably  $10^{-7}$  to  $10^{-3}$  gram-atom/liter.

In the process of the present invention, the amount of the aluminoxane as the catalyst component (B), calculated as the aluminum atom in the reaction system, 15 is not more than 3 milligram-atoms/liter, especially preferably 0.02 to 1 milligram-atom/liter. The proportion of the aluminum atom of the catalyst component (B) based on the total amount of the aluminum atoms of the catalyst component (B) and the catalyst component (C) in 20 the reaction system is usually 5 to 80 %, preferably 10 to 75 %, especially preferably 15 to 70 %. The proportion of the aluminum atom of the catalyst component (C) on the same basis is usually 20 to 95 %, preferably 25 to 90 %, especially preferably 30 to 85 %. In the process 25 of the present invention, the ratio of the total amount of the aluminum atoms in the catalyst component (B) and the catalyst component (C) to the transition metal atom in the reaction system is usually from 20 to 10,000, preferably from 50 to 5,000, especially preferably from 30 100 to 2,000.

The process of the present invention is effectively for the production of olefin polymers, particularly an ethylene polymer and an ethylene-alpha-olefin copolymer. Examples of the olefins that can be utilized 35 in the present invention are ethylene and alpha-olefins having 3 to 20 carbon atoms, such as propylene, 1-butene,

- 13 -

1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicocene. As necessary, polyenes such as diene can be used as a comonomer.

5 In the process of the present invention, olefin polymerization is usually conducted in a gas-phase or in a liquid-phase, for example, in a solution. In the liquid-phase polymerization, an inert hydrocarbon may be used as a solvent. It is also possible to use an olefin 10 itself as the solvent.

Specific examples of the hydrocarbon medium are aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, octane, decane, dodecane, hexadecane and octadecane; alicyclic hydrocarbons such as cyclopentane, 15 methylcyclopentane, cyclohexane and cyclooctane; aromatic hydrocarbons such as benzene, toluene and xylene; and petroleum fractions such as gasoline, kerosene and gas oil.

In the process of the present invention, the 20 polymerization temperature is usually -50° to 200°C, preferably 0° to 120°C. The polymerization pressure is usually atmospheric pressure to 100 kg/cm<sup>2</sup>, preferably atmospheric pressure to 50 kg/cm<sup>2</sup>. The polymerization may be carried out batchwise, semicontinuously or continuously. It is possible to conduct the polymerization 25 in two or more stages having different reaction conditions. The molecular weight of the polymer obtained can be controlled by hydrogen and the polymerization temperature.

The process for olefin polymerization according 30 to the present invention has a feature that the process, as compared with the conventional processes, can produce a polymer having a large molecular weight when it is applied particularly to ethylene polymerization or ethylene-alpha-olefin copolymerization. Further, the process can 35 produce an olefin copolymer having a narrow molecular

- 14 -

weight distribution and a narrow component distribution when it is applied to copolymerization of at least two olefins.

[EXAMPLES]

5 The process of the present invention will now be specifically illustrated by the following examples. The  $\bar{M}_w/\bar{M}_n$  value was measured by the following procedure in accordance with Takeuchi, "Gel Permeation Chromatography", published by Maruzen Co., Ltd.

- 10 (1) By using a standard polystyrene of a known molecular weight (monodisperse polystyrene produced by Toyo Soda Co., Ltd.), the molecular weight M and its GPC (gel permeation chromatograph) count are measured. A calibration curve of the molecular weight M versus EV 15 (elution volume) is prepared. The concentration at this time is adjusted to 0.02 % by weight.

(2) The GPC chromatogram of the sample is taken by GPC, and the number average molecular weight  $\bar{M}_n$  and the weight average molecular weight  $\bar{M}_w$  of the sample 20 are calculated as polyethylene by the procedure (1) above, and the  $\bar{M}_w/\bar{M}_n$  value is determined. The sample preparation conditions and the GPC measurement conditions at this time are as follows.

Sample preparation

- 25 (a) Take the sample together with an o-di-chlorobenzene solvent in an Erlenmeyer flask so that its concentration is 0.1 % by weight.  
(b) Heat the flask to 140°C and for about 30 minutes

30 GPC measurement conditions

The GPC measurement was conducted under the following conditions.

- (a) Device: 150C-ALC/GPC made by Waters Co.  
(b) Column: GMH type made by Toyo Soda Co.,  
35 Ltd.  
(c) Amount of the sample: 400 microliters

- 15 -

- (d) Temperature: 140°C
- (e) Flow rate: 1 ml/min.

The amount of an n-decane-soluble portion in the copolymer (as the amount of the soluble portion is smaller, the narrower is the composition distribution) was measured by adding about 3 g of the copolymer to 450 ml of n-decane, dissolving the copolymer at 145°C, cooling the solution to 23°C, removing the n-decane-insoluble portion by filtration, and recovering the n-decane-soluble portion from the filtrate.

The B value of the ethylenic copolymer of the present invention is defined as follows:

$$B = \frac{P_{OE}}{2P_O \cdot P_E}$$

wherein  $P_E$  represents the molar fraction of the ethylene component in the copolymer,  $P_O$  represents the molar fraction of the alpha-olefin component, and  $P_{OE}$  represents the molar fraction of the alpha-olefin/ethylene sequence in the total dyad sequence.

The B value is an index showing the state of distribution of the individual monomer components in the copolymer chain and is calculated by determining  $P_E$ ,  $P_O$  and  $P_{OE}$  in the above definition in accordance with the papers of G. J. Ray [Macromolecules, 10, 773 (1977)], J. C. Randall [Macromolecules, 15, 353 (1982), J. Polymer Science, Polymer Physics Ed., 11, 275 (1973)], and K. Kimura [Polymer, 25, 441 (1984)]. As the B value is larger, the amount of block-like sequences is smaller and the distribution of ethylene and the alpha-olefin is more uniform. Thus, the copolymer has a narrower composition distribution.

The B value is determined as follows: About 200 mg of the copolymer is uniformly dissolved in 1 ml of

- 16 -

hexachlorobutadiene in a sample tube having a diameter of 10 mm, and a  $^{13}\text{C}$ -NMR spectrum of the sample is taken usually at a temperature of 120  $^{\circ}\text{C}$  under the following conditions.

5 Measuring frequency: 25.05 MHz

Spectral width: 1,500 Hz

Filter width: 1,500 Hz

Pulse repeating time: 4.2 sec

Pulse width: 7 microseconds

10 Number of integrations: 2,000 to 5,000

From the spectrum,  $P_E$ ,  $P_O$  and  $P_{OE}$  are determined, and the B value is calculated from them.

Example 1

Preparation of catalyst component (B)

15 A 400-ml flask purged fully with nitrogen was charged with 37 g of  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$  and 125 ml of toluene. The flask was cooled to 0°C, and 500 millimoles of trimethylaluminum diluted with 125 ml of toluene was added dropwise. The mixture was heated to 40°C, and the

20 reaction was continued at this temperature for 10 hours. After the reaction, the reaction mixture was subjected to solid-liquid separation by filtration. Toluene was removed from the filtrate to obtain 13 g of an aluminoxane as a white solid. It had a molecular weight, as determined by freezing point depression in benzene, of 930. Its m value in the catalyst component [B] was 14.

Preparation of catalyst component (C)

A 400-ml flask purged fully with nitrogen was charged with 4.9 g of  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$  and 125 ml of toluene. The flask was cooled to 0°C, and 200 millimoles of triisobutylaluminum diluted with 125 ml of toluene was added dropwise. The mixture was heated to 40°C, and the reaction was continued at this temperature for 24 hours. After the reaction, the reaction mixture was subjected to solid-liquid separation by filtration. The filtration portion was used in polymerization. The solvent was

- 17 -

removed from the filtrate under reduced pressure to obtain a product. The product had a molecular weight, as determined by freezing point depression in benzene, of 610.

5 Polymerization

500 ml of toluene was fed into a glass autoclave having an internal volume of 1 liter and fully purged with nitrogen, and a mixed gas consisting of ethylene and propylene (120 liters/hr and 80 liters/hr, respectively) was passed through the autoclave and left to stand at 20°C for 10 minutes. Then, 0.25 milligram-atom, as Al atom, of the catalyst component (C) and 0.25 milligram-atom, as Al atom, of the catalyst component (B) were added. Subsequently,  $2.5 \times 10^{-3}$  millimole of bis-(cyclopentadienyl)zirconium dichloride was added, and polymerization was started. The mixed gas consisting of ethylene and propylene was continuously fed, and polymerized at 20°C for 30 minutes under atmospheric pressure. After the polymerization, a small amount of methanol was added to stop the polymerization. The polymer solution was poured into a large excess of methanol to precipitate the polymer. The precipitated polymer was dried at 130°C for 12 hours under reduced pressure. There was consequently obtained 15 g of a polymer having an MFR of 0.35 g/10 min., an ethylene content, as measured by  $^{13}\text{C-NMR}$ , of 82.9 mole %, an  $M_w/M_n$  of 2.35 and a B value of 1.12.

Example 2

Preparation of catalyst component (C)

30 Preparation of catalyst component (C) was conducted under the same conditions as in Example 1 except that the amount of  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$  was changed from 4.9 g to 4.25 g and the reaction time was changed from 24 hours to 5 hours. After the reaction, the reaction mixture was subjected to solid-liquid separation by filtration. The filtrate portion was used in

- 18 -

polymerization. The solvent was removed from the filtrate under reduced pressure to obtain a product. The product had a molecular weight, as determined by freezing point depression in benzene, of 440.

5 Polymerization

Polymerization was conducted under the same conditions as in Example 1 to obtain 13 g of a polymer having an MFR of 0.30 g/10 min., an ethylene content, as measured by  $^{13}\text{C-NMR}$ , of 82.1 mole %, an  $\bar{M}_w/\bar{M}_n$  of 2.32 and a B value of 1.14.

10 Examples 3 to 5 and Comparative Example 1

Preparation of catalyst component (C)

Preparation of catalyst component (C) was conducted under the same conditions as in Example 1 except that the triisobutylaluminum used in Example 1 was changed to tri(2-methylpentyl)aluminum, tri(2-ethylhexyl)aluminum, isoprenylaluminum and tri-n-butyl-aluminum.

Polymerization

20 Polymerization was conducted in the same conditions as in Example 1. The results are shown in Table 1.

Table 1

Example or Comparative Example	Preparation of component (C)	Result of polymerization				
		Yield g	MFR g/10 min.	Ethylene content mole %	$\bar{M}_w/\bar{M}_n$	B value
Example 3	Tri(2-methylpentyl)aluminum	14.5	0.34	82.0	2.25	1.13
Example 4	Tri(2-ethylhexyl)aluminum	14.8	0.30	80.6	2.06	1.15
Example 5	Isoprenylaluminum	10.2	0.53	83.0	2.26	1.12
Comparative Example 1	Tri-n-butylaluminum	0.5	-	-	-	-

- 20 -

## Example 6

Polymerization

250 ml of hexane and 750 ml of 4-methyl-1-pentene were fed into a stainless steel autoclave having an internal volume of 2 liters and fully purged with nitrogen. The contents in the autoclave was heated to 35°C. Then, the catalyst component (B) of Example 1, the catalyst component (C) of Example 2 and bis(cyclopenta-dienyl)zirconium dichloride were fed into the autoclave in amounts of 0.5 milligram-atom, 0.5 milligram-atom (both as Al atom) and 0.001 millimole, respectively. Subsequently, ethylene was introduced and polymerization was started. Ethylene was continuously fed so that the total pressure was maintained at 8 kg/cm<sup>2</sup>G. The polymerization was conducted at 45°C for 1 hour. After the polymerization, a small amount of methanol was added to stop the polymerization. Then, the whole reaction mixture was poured into a large excess of methanol to recover a polymer. The crude polymer was dried at 80°C for 12 hours under reduced pressure to obtain a polymer. The yield was 30.1 g. The polymer had an MFR of 0.24 g/10 min., a density of 0.901 g/cm<sup>3</sup> and an  $\bar{M}_w/\bar{M}_n$  of 2.75. The weight fraction of the decane-soluble portion at room temperature in the polymer was 1.8 % by weight.

## 25 Example 7

Polymerization

500 ml of toluene was fed into a stainless steel autoclave having an internal volume of 2 liters and fully purged with nitrogen. Then, the catalyst component (B) and the catalyst component (C) prepared in Example 1 were fed into the autoclave in amounts, as Al atom, of 1 milligram-atom and 2 milligram-atoms, respectively. Thereafter, 250 ml of liquid propylene was fed into the system. Subsequently, 0.001 millimole of ethylene(bis-indenyl)zirconium dichloride was added at -10°C, and polymerization was conducted at -10°C for 6 hours. After

- 21 -

6 hours, a small amount of methanol was added to the system to stop the polymerization. Propylene was removed by reducing the pressure from the polymerization system. The resulting toluene slurry of polymer was poured to a 5 large amount of methanol to recover a polymer. The crude polymer was dried at 80°C under reduced pressure to obtain 48.1 g of a polypropylene. It had a viscosity  $\eta_1$ , as measured in decalin at 135°C, of 0.97 dl/g.

Example 8

---

10 Polymerization

500 ml of hexane and 500 ml of 4-methyl-1-pentene were fed into a stainless steel autoclave having an internal volume of 2 liters and fully purged with nitrogen. The contents in the autoclave was heated to 15 55°C. Then, the catalyst component (C) of Example 2 was fed into the autoclave in an amount of 1 milligram-atom as Al atom. There was further fed into the autoclave 0.25 ml of a toluene solution obtained by contacting the catalyst component (B) of Example 1 and bis(cyclopenta-20 dienyl)zirconium dichloride of respective concentrations of 0.4 gram-atom/liter as Al atom and 0.012 gram-atom/-liter as Zr atom at 20°C for 30 minutes. Thereafter, ethylene was introduced and polymerization was started. Ethylene was continuously fed so that the total pressure 25 was maintained at 7 kg/cm<sup>2</sup>, and the polymerization was conducted at 60°C for 1 hour. After the polymerization, a small amount of methanol was added to stop the polymerization. The reaction mixture was poured into a large excess of methanol to recover a polymer. The crude 30 polymer was dried at 80°C for 12 hours under reduced pressure to obtain a polymer. The yield was 33.6 g. The polymer had an MFR of 0.18 g/10 min., a density of 0.903 g/cm<sup>2</sup> and an  $\bar{M}_w/\bar{M}_n$  of 2.83. The weight fraction of the decane-soluble portion at room temperature in the polymer 35 was 1.3 % by weight.

- 22 -

## SCOPE OF CLAIM FOR PATENT

1. A process for polymerizing olefins, characterized by polymerizing or copolymerizing olefins in the presence of a catalyst composed of

- (A) a compound of a transition metal of Group IVB of the periodic table,
- (B) an aluminoxane produced from trimethylaluminum, and
- (C) an aluminoxane wherein at least one hydrocarbon group other than n-alkyl groups is bonded to an aluminum atom.

2. The process set forth in claim 1, wherein the transition metal of Group IVB of the periodic table of the compound (A) is titanium, zirconium or hafnium.

3. The process set forth in claim 1, wherein the aluminoxane produced from trimethylaluminum is represented by the following formula (II)



wherein M is a number of 2 or larger, or the following formula (III)



wherein m has the same definition as given above.

4. The process set forth in claim 1, wherein the hydrocarbon group of the aluminoxane (C) in which at least one hydrocarbon group other than n-alkyl groups is bonded to an aluminum atom is a branched alkyl group, a cycloalkyl group or an aryl group.

5. The process set forth in claim 1, wherein the

- 23 -

compound (A) is used in such an amount that the concentration of the transition metal of said compound in the polymerization reaction system becomes  $10^{-8}$  to  $10^{-2}$  gram-atom/liter.

6. The process set forth in claim 1, wherein the aluminoxane (B) is used in such an amount that the concentration of the aluminum atom of the aluminoxane (B) in the polymerization reaction system becomes 3 milligram-atoms/liter or below.

7. The process set forth in claim 1, wherein the aluminoxane (C) is used in such a proportion that the amount of the aluminum atom of the aluminoxane (C) becomes 20-95 % of the total amount of the aluminum atoms of the aluminoxane (C) and the aluminoxane (B).

## INTERNATIONAL SEARCH REPORT

International Application No. PCT/JP87/00898

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) <sup>3</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl<sup>4</sup> C08F10/00, C08F4/64

## II. FIELDS SEARCHED

Minimum Documentation Searches <sup>4</sup>

Classification System	Classification Symbols
IPC	C08F10/00, C08F110/00, C08F210/00, C08F4/64

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>

III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>6</sup>

Category <sup>7</sup>	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
A	JP, A, 60-260602 (Idemitsu Kosan Co., Ltd.) 23 December 1985 (23. 12. 85) Claim, (Family: none)	1-7
A	JP, A, 60-130604 (Idemitsu Kosan Co., Ltd.) 12 July 1985 (12. 07. 85) Claim, (Family: none)	1-7
A	JP, A, 58-19309 (Hoechst A.G.) 4 February 1983 (04. 02. 83) Claim, & US, A, 4,542,199	1-7

<sup>6</sup> Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claims or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

<sup>7</sup> later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<sup>8</sup> document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step<sup>9</sup> document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art<sup>10</sup> document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search <sup>11</sup>

December 8, 1987 (08.12.87)

Date of Mailing of this International Search Report <sup>12</sup>

December 21, 1987 (21.12.87)

International Searching Authority <sup>13</sup>

Japanese Patent Office

Signature of Authorized Officer <sup>14</sup>